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Sepiolite functionalized with *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine triacetic acid trisodium salt. Part II: Sorption of Ni^{2+} from aqueous solutions

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Abstract: The sorption of Ni^{2+} on sepiolite functionalized by covalent grafting of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt, MSEAS, was studied in batch experiments as a function of the initial metal concentration, the equilibration time, the pH value and the temperature. The modification of sepiolite resulted in enhanced Ni^{2+} retention with a capacity of 0.261 mmol g^{-1} at 298 K. The retention of Ni^{2+} occurred dominantly by specific sorption and exchange of Mg^{2+} from the sepiolite structure. The sorption process followed pseudo-second-order kinetics. The sorption equilibrium results were best described by the non-linear form of the Langmuir sorption equation. The values of the thermodynamic parameters (changes of enthalpy, free energy and entropy) were calculated from temperature dependent sorption isotherms and their values showed that the sorption of Ni^{2+} onto modified sepiolite was endothermic.

Keywords: functionalized sepiolite; sorption; Ni^{2+}; kinetics; thermodynamics.

INTRODUCTION

Water pollution by heavy metals is a serious environmental problem with harmful impacts on the ecological balance and living organisms, including humans. The major contributors to the high concentrations of Ni^{2+} in aqueous media are the industries related to stainless steel, electroplating, jewelry, coinage, catalysts, batteries and accumulators. Even at low concentrations, nickel has a damaging effect on human health because it accumulates in the lungs, kidneys, liver, intestines and heart. Higher concentrations of nickel cause various diseases and disorders, including cancer of the lungs, nose and bone, chronic headaches, sleeplessness and diarrhea.[1] Therefore, the removal of Ni^{2+} from water and

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wastewaters, in order to reduce its concentration to below the acceptable range, is highly warranted.

The remediation of heavy metals using a sorption technique is now progressing through numerous researches aimed at the development of highly efficient, cost effective, and environmentally friendly materials as sorbents. The study of sorption kinetics is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. Three stages are considered to be involved during the sorption of metal ions onto sorbents: 1) transfer of the sorbate molecules from the bulk solution to the solid surface, *i.e.*, film diffusion; 2) intraparticle diffusion within the interior of the sorbent and 3) sorption of the sorbate on active sites (physisorption or chemisorption).[2] The sorption capacity and the kinetics for metal uptake from the liquid phase depends on several physicochemical factors related to the sorbent (*e.g.*, porosity, specific area and particle size, the sorbate (*e.g.*, ionic radius and coordination number) and the liquid phase characteristics, including the solution pH, temperature, initial metal concentration in the solution and the presence of other cations.

In order to improve its sorption performance for heavy metal ions, sepiolite was first functionalized using different silane coupling agents. Modification of sepiolite was performed using triethoxy-3-(2-imidazolin-1-yl)propylsilane in toluene solution and the capacity of the material for Co^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+} sorption was investigated.[3] Liang *et al*. showed that the sorption capacities of mercaptopropyltrimethoxysilane-functionalized sepiolite for Pb^{2+} and Cd^{2+} were higher than those of natural sepiolite.[4] The surface modification of sepiolite with [3-(2-aminoethylamino)propyl]trimethoxy-silane and its ability to sorb cations was investigated.[5] The sorption capacity of the modified sepiolite was higher for zinc, copper and cobalt than for the other ions because of specific interactions between the metal ions and the amine groups.

The removal of Cr(VI) from aqueous solution using adsorbents obtained by covalent grafting of (3-mercaptopropyl)trimethoxy-silane and [3-(2-aminoethylamino)propyl]trimethoxy-silane onto natural, acid activated and thermo-acid activated sepiolites was studied.[6–8] The adsorption capacities of amine-functionalized sepiolites for chromium(VI) sorption were much higher than those of mercapto–silane-functionalized sepiolites under the same conditions.

The first part of this study, the modification of sepiolite with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt in order to obtain an efficient sorbent for water treatment and the characterization of the prepared sorbent, was reported previously.[9] In continuation, the adsorption properties of the functionalized sepiolite sample for the sorption of Ni^{2+} are discussed herein.

The batch sorption technique was used to obtain sorption isotherms and to explore the effects of temperature, the initial pH value and the equilibration time on the sorption capacity. The capabilities of the Langmuir, Freundlich and Red-

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lich–Peterson isotherm models to fit the equilibrium sorption data were investigated, while the pseudo-first, pseudo-second order and intraparticle diffusion models were used to fit the kinetic sorption data.

EXPERIMENTAL

Materials

The functionalization of sepiolite was performed from aqueous solution using of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt ($(CH_3O)_3Si(CH_2)_3N$-$(CH_2COONa)N(CH_2)_2N(CH_2COONa)_2$), MSEA, Gelest).[9] The results of the morphological characterization, X-ray diffraction, FTIR and DTA analyses, determination of the specific surface areas and pore size distribution using the BET method and the point of zero charge (pH_{pzc}) of the MSEA-functionalized sepiolite (MSEAS) were reported previously.[9]

Determination of the point of zero charge of the MSEAS in solutions of Ni^{2+}

The shift in the point of zero charge was investigated by the batch equilibration method, using 0.01 and 0.001 mol dm^{-3} solutions of $Ni(NO_3)_2$ at different initial pH values (pH_i), ranging from ~3.5 to ~8.0 using the batch equilibration method described elsewhere.[10] Equilibration was attained by shaking for 24 h in a water bath thermostated at 298 K. The concentrations of Ni^{2+} and Mg^{2+} in the solutions after equilibration with 0.001 mol dm^{-3} solutions of $Ni(NO_3)_2$ were measured. The quantity of sorbed Ni^{2+} was calculated in order to determine the effect of the initial pH value on the sorption process.

Sorption procedure

All sorption experiments were conducted using the batch equilibration technique in Ni^{2+} solutions prepared in demineralized water. A series of 25 cm^3 of each solution containing 0.05 g of sorbent in poly(vinyl chloride) (PVC) vessels were shaken in a water bath thermostated at the desired temperature. The dispersions were filtered and the initial Ni^{2+} concentration and metal ion remaining non-adsorbed in the supernatant, as well as the concentration of Mg^{2+} were determined using atomic absorption spectroscopy (AAS). All the sorption studies were repeated twice and the reported value is the average of the two measurements.

The following conditions were maintained for different sets of experiments:

– Effects of pH: initial concentration of Ni^{2+} 0.01 and 0.001 mol dm^{-3}, pH values from ~3.5 to ~8, an equilibration period of 24 h and a temperature of 298 K.

– Isotherms: initial concentration of Ni^{2+} between 25 and 200 mg dm^{-3}, pH values of the solutions 5.6±0.1, an equilibration period of 24 h and a temperature of 298 K.

– Kinetics: initial ion concentration of 100 mg dm^{-3}, pH value of 5.6±0.1, temperature of 298 K, contact times ranging from 1 h to 24 h. The final concentrations of Ni^{2+} and Mg^{2+} were measured in the supernatant as dependent variables of time.

– Thermodynamics: initial concentration of Ni^{2+} between 25 and 200 mg dm^{-3}, pH values of the solutions 5.6±0.1, equilibration period of 24 h, temperatures of 318, 328 and 338 K.

RESULTS AND DISCUSSION

Determination of the point of zero charge of the MSEAS in solutions of Ni^{2+}

As a result of specific sorption on the sorbent surface that lowers the number of sites available for the sorption of H^+, the pH_{pzc} in Ni^{2+} solutions were shifted to lower values compared with those obtained in KNO_3 solutions.[11] From the dependences pH_f *vs*. pH_i, (Fig. 1a) it can be seen that the pH_{pzc} of the modified

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sepiolite were 5.6±0.1 for 0.01 mol dm^{-3} and 5.8±0.1 for 0.001 mol dm^{-3} $Ni(NO_3)_2$. The pH_{pzc} was also lower compared with values obtained for natural sepiolite in Ni^{2+} solutions (6.5±0.1 for 0.01 mol dm^{-3} and 6.8±0.1 for 0.01 mol dm^{-3} $Ni(NO_3)_2$)[12] due to the presence of additional groups originating from the modifier located on the external sites of the sepiolite, which interact with Ni^{2+} by forming stable surface complexes. In this way, the quantity of specifically sorbed Ni^{2+} was increased.

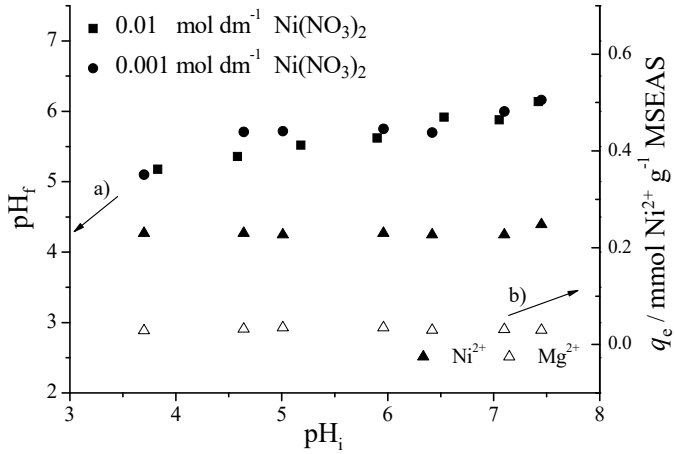

Fig. 1. a) Dependences of pH_f on pH_i during the equilibration of MSEAS in 0.01 mol dm^{-3} and 0.001 mol dm^{-3} $Ni(NO_3)_2$ solutions; b) effect of initial pH on the amount of Ni^{2+} sorbed on MSEAS and quantity of ion exchanged Mg^{2+}.

The quantities of sorbed Ni^{2+} from 0.001 mol dm^{-3} $Ni(NO_3)_2$ solution at different pH values and the amounts of Mg^{2+} present in the solutions as result of ion exchange are shown in Fig. 1b. The sorption of Ni^{2+} was examined in the pH range from ~3.5 to ~8.0, in order to avoid ion hydrolysis at higher pH values and the dissolution of sepiolite at lower pH values.

Effect of the initial pH value

The solution pH can have a significant effect on the uptake of metal, since it determines the surface charge of the sorbent and the degree of ionization and speciation of the sorbate. The effect of initial pH on the sorption of Ni^{2+} by modified sepiolite sorbent was observed at different pH (3.5–8.0) simultaneously with determination of point of zero charge of the MSEAS in solutions of Ni^{2+}. To prevent the precipitation of Ni^{2+} from solution at high pH values, the solution pH was maintained at pH less than the pH of precipitation formation.

The quantity of exchangeable Mg^{2+} was determined as the difference between the total amount and the amount of Mg^{2+} released into the solution by the dissolution (0.05 mmol g^{-1} MSEAS). The amount of nickel ion sorbed per

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unit mass of MSEAS was almost constant, amounting to ~0.032 mmol Ni^{2+} g^{-1} MSEAS. It is obvious that the change in the initial pH value of the metal ion solutions in the investigated range did not affect a change in the sorption capacity.

The quantity of Mg^{2+} released into the solution during the ion exchange process with Ni^{2+} was also almost constant at different pH values, meaning that the process of ion exchange was of the same intensity. During the ion exchange process, Mg^{2+} are displaced from the MSEAS lattice and released into solution. The ion exchange process was also confirmed during investigation of effect of contact time on the amounts of Ni^{2+} sorbed (Fig. 3, later on). This process does not influence a change in the pH_{pzc} because H^+ are not involved in the ion exchange process.

The final pH values determined during the pH_{pzc} determination were similar for all the investigated initial pH values, *i.e.*, the process of the specific sorption of Ni^{2+} onto MSEAS in this pH range was not significantly affected by the pH value. Due to the simultaneously occurring specific sorption and ion exchange, as the main mechanisms of sorption, the total amount of metal ion sorbed per unit mass of MSEAS remained almost constant in the investigated pH range.

Sorption isotherm studies and modeling

The amount of nickel ions sorbed onto MSEAS at 25 °C at a pH_i of 5.6±0.1, and the dependence of the quantity of Mg^{2+} ion exchanged as functions of the equilibrium concentration are shown in Fig. 2.

According to Fig. 2, the modified sample had a higher sorption capacity (~0.24 mmol g^{-1} MSEAS) than the natural sepiolite (≈0.20 mmol g^{-1} SEP),[12] *i.e.*, an improvement of the sorption efficiency was accomplished by modification with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt from an aqueous solution. Nickel sorption on the natural sepiolite sample was attributed to cation exchange and the formation of surface complexes through Si–OH groups. When a dispersion of natural sepiolite was treated with a silane solution, the reactive silanol groups exhibit a high affinity for –Si–OH groups on the sepiolite surface thereby forming –Si–O–Si–bonds and retaining three free $–COO^-$ groups. Vasiliev *et al*. investigated metal complexes based on grafted *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid onto silica by nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy and showed that metals form several complexes with the carboxyl groups of the ligand.[13] These complexes have different structures with a different degree of substitution of the water molecules on the ligand in the plane of the coordination sphere.

The amount of Mg^{2+} exchanged (Fig. 2) increased with increasing amount of Ni^{2+} sorbed on the mineral, which corroborates ion exchange, *i.e.,* replacement of Mg^{2+} on the edges of the octahedral layer of sepiolite with Ni^{2+}, as one of the

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main mechanisms of sorption. It can be seen that the MSEAS had a slightly lower ion exchange capacity for Ni^{2+} than the natural sepiolite sample.[12] Grafting of organosilanes on sepiolites is limited to the external surface of sepiolite.[14] The Mg–OH groups at the edges of the sepiolite channels responsible for ion exchange with metal cations from solution remain unaffected by the process of silane functionalization. In this way, the ion exchange capacity remained and was similar to that of natural sepiolite. The increase in Ni^{2+} sorption on the functionalized sepiolite could be explained by an increase in specific sorption, *i.e.*, the interaction of both surface silanol groups and additional groups originating from the modifier, which exhibit a high binding affinity toward Ni^{2+}.

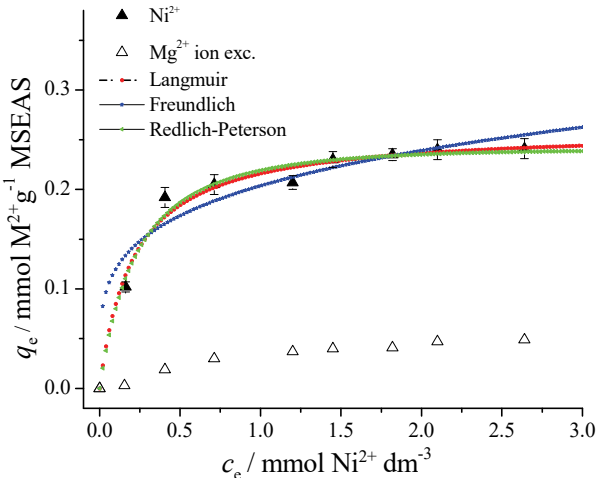

Fig. 2. Sorption isotherm for Ni^{2+} onto MSEAS and the dependence of q_e (mmol Mg^{2+} g^{-1}) on c_e (mmol Ni^{2+} dm^{-3}) and the fitting of the experimental data to different isotherm models.

The equilibrium sorption data were analyzed by three isotherm models: Langmuir, Freundlich and Redlich−Peterson, using nonlinear fitting (presented in Fig. 2).

The Langmuir model[15] assumes monolayer sorption at specific homogeneous sites, with no interactions between the sorbed species. The Freundlich equation[16] describes sorption (possibly multilayer in nature) on a heterogeneous surface consisting of non-identical and energetically non-uniform sites. The Redlich−Peterson model[17] is represented by a three-parameter, empirical equation featuring both Langmuir and Freundlich isotherms. This model approaches the Freundlich isotherm model at high concentrations (when β is equal to 0) and predicts behaviors corresponding to the Langmuir form at the low concentration limits (when the β values are close to 1). The sorption isotherms constants for Ni^{2+} sorption onto MSEAS, determined by non-linear regression analysis using the Easy Plot, are summarized in Table I.

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TABLE I. Sorption parameters and coefficients of correlation according to the Langmuir, Freundlich and Redlich–Peterson models for the sorption of Ni^{2+} ions onto MSEAS at 298 K

Langmuir $q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$			Freundlich $q_e = K_f c_e^{1/n}$			Redlich–Peterson $q_e = \frac{K_R c_e}{1 + a_R (c_e)^{\beta}}$			
K_L / $dm^3\ mmol^{-1}$	q_m / $mmol\ g^{-1}$	R^2	K_f / $mmol^{1-1/n}\ dm^{3/n}\ g^{-1}$	n	R^2	K_R / $dm^3\ g^{-1}$	a_R / $(dm^3\ mmol^{-1})^{\beta}$	β	R^2
4.77	0.261	0.984	0.204	4.33	0.954	1.06	3.86	1.04	0.985

According to presented results, both the Langmuir and Redlich–Peterson isotherms showed better correlation with the experimental data than the Freundlich isotherm, as expressed by the higher correlations coefficients. Figure 2 shows that the Langmuir and the Redlich–Peterson isotherms overlapped one another. The value of the Redlich–Peterson parameter β was close to 1, indicating that the Redlich–Peterson isotherm adopts the Langmuir isotherm, and that experimental data for sorption of Ni^{2+} onto the modified sepiolite sample could be best described by the Langmuir sorption model. The results of the isotherm modeling indicate monolayer coverage of the MSEAS by Ni^{2+} and a homogenous distribution of the active sites on the MSEAS surface.

Effect of contact time

The kinetics of Ni^{2+} sorption on the MSEAS at 100 mg dm^{-3} initial Ni^{2+} concentration at a temperature of 298 K is illustrated in Fig. 3. The sorption of Ni^{2+} was initially fast with >80 % of Ni^{2+} sorbed in the first 60 min. This initial rapid sorption was followed by a much slower period. After 1000 min, an apparent equilibrium was achieved. In addition to Ni^{2+} sorption, the quantity of Mg^{2+} released into the solution, resulting the ion exchange process, was also examined and a similar dependence was registered.

In addition to equilibrium isotherms, information on sorbate transport is essential for analyzing the dynamic behavior of sorption. Three kinetic models were employed to describe the mechanism of sorption on the modified sepiolite: the pseudo-first-order equation proposed by Lagergren,[18] the pseudo-second--order kinetic model proposed by Blanchard *et. al.*,[19] and the intraparticle diffusion model proposed by Weber and Morris.[20] The rate constant k_1 in min^{-1} was calculated from the slope of the ln $(q_e - q_t)$ *vs.* t plot, and the second-order rate constant k_2 in g $mmol^{-1} \cdot min^{-1}$ and the equilibrium sorption capacity, q_e, from linear plot of t/q_t *vs.* t, by considering the values of the slope and the intercept, respectively.

For pure intraparticle diffusion to occur, the plot of q_t *vs.* $t^{1/2}$ should be linear passing through the origin. However, if the plot shows multilinearity, then

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the sorption process may be controlled by a combination of film and intraparticle diffusion, *i.e.* more than one-step is involved in the sorption process.

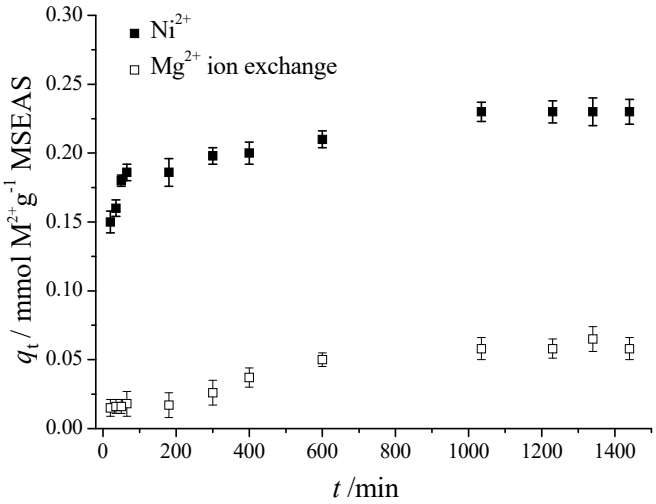

Fig. 3. Effect of contact time on the amounts of Ni^{2+} sorbed onto MSEAS and Mg^{2+} exchanged (c_i = 100 mg dm^{-3}, at a temperature of 298 K and pH of 5.6 ± 0.1).

The values of k_i (intra-particle diffusion rate constant, mmol g^{-1}·min^{-1}) and the constant C were calculated by extrapolation of the second portion of the curve q_t *vs.* $t^{1/2}$ back towards the y-axis. Intraparticle diffusion was not the only rate--limiting step because the plot did not pass through the origin.

The results presented in Table II show that the pseudo-second-order model fitted the sorption data much better than the pseudo-first-order and intraparticle diffusion models. The pseudo-second-order rate law expression is based on the assumption that the rate-limiting step is chemical sorption, which is in agreement with the finding that the main mechanisms of sorption of Ni^{2+} onto MSEAS are chemical processes: specific sorption and ion exchange of Mg^{2+} from the sepiolite structure with Ni^{2+} from the solutions.

TABLE II. Kinetic parameters for Ni^{2+} sorption onto MSEAS

Pseudo-first-order			Pseudo-second-order				Intra-particle diffusion		
$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$			$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$				$q_t = k_i t^{1/2} + C$		
k_1 min^{-1}	q_e mmol g^{-1}	R^2	k_2 g mmol^{-1} min^{-1}	q_e mmol g^{-1}	R^2	h mol g^{-1} min^{-1}	k_i mmol g^{-1} min$^{-1/2}$	C mmol g^{-1}	R^2
0.0029	0.077	0.950	0.124	0.236	0.998	0.0069	0.169	0.0016	0.916

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Many investigations demonstrated that the kinetic behavior of heavy metal sorption studies are satisfactorily explained with the pseudo-second-order sorption equation.[21–23] This trend suggests that the rate-limiting step in heavy metal sorption is chemisorption, which involves valence forces through sharing or exchange of electrons between sorbent and sorbate, complexation, coordination and/or chelation, rather than physisorption.

Effect of temperature

The effect of temperature on the sorption of nickel ions onto modified sepiolite is shown in Fig. 4. In the experimental temperature range, the quantity of nickel ions sorbed by MSEAS increased with increasing temperature, demonstrating that the process of nickel sorption is endothermic. Non-linear fitting of experimental data for Ni^{2+} sorption onto MSEAS using the Langmuir isotherm at various temperatures are also seen in Fig. 4. The values of the sorption parameters and coefficients of correlation (given in Table III) confirmed that the Langmuir isotherm equation not only represents the sorption process at 298 K very well, but also in the temperature range 318–338 K.

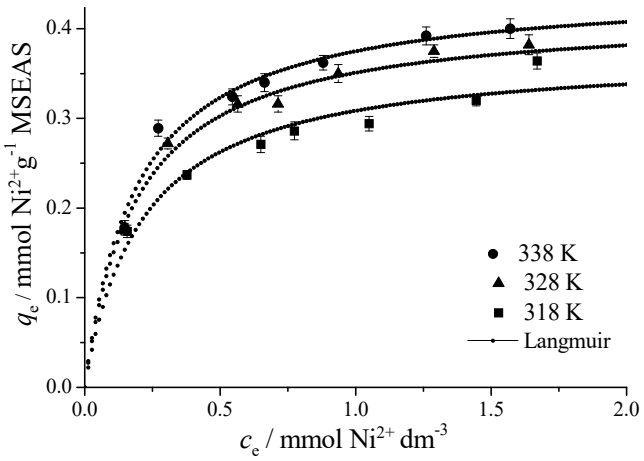

Fig. 4. Sorption isotherms for the sorption of Ni^{2+} onto MSEAS at different temperatures.

TABLE III. Sorption parameters and coefficients of correlation according to the Langmuir model for the sorption of Ni^{2+} ions onto MSEAS at different temperatures

T / K	Parameter		
	R^2	q_m / mmol g^{-1}	$K_L \times 10^{-3}$ / dm^3 mol^{-1}
318	0.980	0.374	4.71
328	0.995	0.425	5.10
338	0.970	0.460	5.24

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In order to understand the sorption process from the aspect of energy change, the enthalpy change (ΔH, kJ mol^{-1}) and entropy change (ΔS, J mol^{-1} K^{-1}) were determined graphically from the slope and intercept, respectively, of the straight line obtained by plotting ln K_L *vs*. $1/T$, using approach of Liu.[24] The values of the obtained thermodynamic parameters, ΔH and ΔS, and Gibbs free energy change (ΔG, kJ mol^{-1}, calculated using the equation $\Delta G = -RT \ln K_L$) are listed in Table IV.

TABLE IV. Thermodynamic parameters for the sorption of nickel ions onto MSEAS

ΔH / kJ mol^{-1}	ΔS / J mol^{-1} K^{-1}	ΔG / kJ mol^{-1}			
		298 K	318 K	328 K	338 K
2.08	77.1	–20.92	–24.80	–25.60	–26.37

The Gibbs free energy change (ΔG) indicates the degree of spontaneity of a sorption process and the greater the negative value is, the more energetically favorable is the sorption. For all the investigated temperatures, the ΔG values were negative. The value of ΔG became more negative with increasing temperature, indicating that the spontaneous nature of the adsorption of Ni(II) was proportional to the temperature. Such a dependence of ΔG on temperature and the positive ΔH values confirmed the endothermic nature of sorption of Ni^{2+} onto MSEAS. The ΔS value was calculated to be 78.0 J mol^{-1} K^{-1}, which, on the one hand, showed the affinity of the sorbent for Ni^{2+} and, on the other hand, indicated the increase in randomness at the solid/liquid interface after sorption.[25]

The positive ΔS value arose because of the redistribution of energy between the adsorbate and the adsorbent. Before the adsorption occurred, the heavy metal ions near the surface of the adsorbent are more ordered than in the adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent is higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules increases with increasing adsorption thereby producing a positive value of ΔS.[21]

CONCLUSIONS

The sorption capacity shown by sepiolite functionalized with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt for Ni^{2+} from aqueous solutions was higher than that of the natural sepiolite sample, suggesting that this modification process is an effective method for obtaining a sorbent for the removal of Ni^{2+} from highly polluted waters. The equilibrium sorption data were adequately described by the Langmuir isotherm equation.

The retention of Ni^{2+} occurred dominantly by specific sorption and exchange of Mg^{2+} from the sepiolite structure. The kinetic study of the sorption showed that the pseudo-second-order model best described the experimental

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data, indicating that the sorption may be controlled by chemical sorption and that chemisorption might be the rate-limiting step that controls the sorption process.

The amount of Ni^{2+} sorbed onto the modified sepiolite increased with increasing temperature. The thermodynamics of the sorption indicate the endothermic and spontaneous nature of sorption process. On the contrary, the sorption capacity was not significantly changed on changing the initial pH value.

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ИЗВОД

ФУНКЦИОНАЛИЗАЦИЈА СЕПИОЛИТА ПРИМЕНОМ СОЛИ НАТРИЈУМА *N*-[(3-ТРИМЕТОКСИ)ПРОПИЛ]ЕТИЛЕНДИАМИНТРИАЦЕТАТНЕ КИСЕЛИНЕ. ДЕО II: СОРПЦИЈА ЈОНА НИКЛА ИЗ ВОДЕНИХ РАСТВОРА

СЛАВИЦА С. ЛАЗАРЕВИЋ, ИВОНА М. ЈАНКОВИЋ-ЧАСТВАН, БОЈАН М. ЈОКИЋ, ЂОРЂЕ Т. ЈАНАЋКОВИЋ и РАДА Д. ПЕТРОВИЋ

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У раду је испитана ефикасност уклањања јона никла из водених раствора на сепиолиту који је модификован применом натријумове соли *N*-[(3-триметокси)пропил]етилендиаминтриацетатне киселине (MCEAC). Испитан је утицај почетне концентрације јона никла, времена уравнотежавања, pH вредности и температуре на процес сорпције применом методе уравнотежавања посебних проба. Поступак модификације природног сепиолита довео је до пораста капацитета сорпције јона никла. Сорпција је последица истовременог одигравања процеса специфичне сорпције и јонске измене са јонима магнезијума из структуре сепиолита. Поређењем експерименталних резултата са три модела сорпционих изотерми утврђено је да се процес сорпције јона никла на модификованом сепиолиту може описати моделом Langmuir сорпционе изотерме. Испитивање кинетике сорпције показало је да се процес сорпције у складу са кинетичким моделом псеудо-другог реда. Вредности термодинамичких параметара (промене енталпије, ентропије и слободне енергије сорпције) одређене на основу зависности сорпције од температуре, указују на то да је процес сорпције јона никла на узорку MCEAC ендотерман.

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REFERENCES

1. R. P. Beliles, *The Lesser Metals*, in *Toxicity of Heavy Metals in the Environment*, Marcel Dekker Inc., New York, 1979
2. M. F. Brigatti, C. Lugli, L. Poppi, *Appl. Clay Sci.* **16** (2000) 45
3. Y. Turhan, P. Turan, M. Dogan, M. Alkan, H. Namli, O. Demirbas, *Ind. Eng. Chem. Res.* **47** (2008) 1883
4. X. Liang, Y. Xu, G. Sun, L. Wang, Y. Sun, Y. Sun, X. Qin, *Chem. Eng. J.* **174** (2011) 436
5. M. Dogan, Y. Turhan, M. Alkan, H. Namli, P. Turan, O. Demirbas, *Desalination* **30** (2008) 248
6. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, A. Bjelajac, Dj. Janaćković, R. Petrović, *Hem. Ind.* **67** (2013) 715

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7. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, Dj. Janaćković, R. Petrović, *Appl. Clay. Sci.* **80**–**81** (2013) 202
8. V. Marjanović, S. Lazarević, B. Potkonjak, Dj. Janaćković, R. Petrović, *Chem. Eng. J.* **166** (2011) 198
9. S. Lazarević, I. Janković-Častvan, B. Jokić, Dj. Janaćković, R. Petrović, *J. Serb. Chem. Soc.* **80** (2015) 1193
10. S. Milonjic, A. Ruvarac, M. Susic, *Thermochim. Acta* **11** (1975) 261
11. N. Kallay, V. Hlady, J. Jednačak-Bišćan, S. Milonjić, in *Physical Methods of Chemistry Series*, Wiley, New York, 1993, p. 73
12. S. Lazarević, I. Janković-Častvan, V. Djokić, Ž. Radovanović, Dj. Janacković, R. Petrović, *J. Chem. Eng. Data* **55** (2010) 5681
13. A. N. Vasiliev, L. V. Golovko, V. V. Trachevsky, G. S. Hall, J. Khinast, *Micropor. Mesopor. Mat.* **118** (2009) 251
14. G. Tartaglione, D. Tabuani, G. Camino, *Micropor. Mesopor. Mat.* **107** (2008) 161
15. I. Langmuir, *J. Am. Chem. Soc.* **40** (1918) 1361
16. H. M. F. Freundlich, *J. Phys. Chem.* **57** (1906) 385
17. O. Redlich, D. L. Peterson, *J. Phys. Chem.* **63** (1959) 1024
18. S. Lagergren, K. Sven. *Vetenskapsakad. Hand*. **24** (1898) 1
19. G. Blanchard, M. Maunaye, G. Martin, *Water Res*. **18** (1984) 1501
20. W. J. Weber Jr., J. C. Morris, *J. Sanit. Eng. Div. Amer. Soc. Civil Eng.* **89** (1963) 31
21. A. R. Kul, H. Koyuncu, *J. Hazard. Mater.* **179** (2010) 332
22. A. Oliveira, L. Coelho, S. Gomes, I. Costa, M. Fonseca, K. de Sousa, J. Espinola, E. da Silva Filho, *Water Air Soil Pollut.* **224** (2013) 1687
23. S. Wan, Z. Ma, Y. Xue, M. Ma, S. Xu, L. Qian, Q. Zhang, *Ind. Eng. Chem. Res.* **53** (2014) 3629
24. Y. Liu, *J. Chem. Eng. Data* **54** (2009) 1981
25. H. Baker, *Desalination* **244** (2009) 48.

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